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Cracking in a Downer Reactor

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Tang and Wei: Waste Edible Oil Fluid Catalytic Cracking in a Downer Reactor

WASTE EDIBLE OIL FLUID CATALYTIC CRACKING IN A DOWNER REACTOR

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ABSTRACT

The waste edible oil used as feedstock of a downer fluid catalytic cracking process (FCC), an environment friendly process to produce clean fuel and high-value chemical materials, was studied in a small hot model of downer reactor. The process has the similar product distribution to petroleum-based fuel fluid catalytic cracking process. And the desired products with trace sulfur contents have the similar molecular weight and chemical structure to the gasoline and diesel from petroleum-based fuel. Therefore, the waste edible oil fluid catalytic cracking is a promising process, with both economic and environmental benefit.

INTRODUCTION

The waste edible oil which is mainly from the catering trade is a kind of fluid with high viscosity and acid value. The annual generation of waste edible oil in US is about 4.54~11.35 Million tons(1); in Japan is 0.4 MT(2); in the European Union is 0.71MT(3); in China is more than 1.2 MT(4). Thus, how to treat the waste edible oil becomes one of the focuses to academic community, government and public. Nowadays, there are mainly three methods to treat the waste edible oil: first as the feeds for animal or the cooking oil for food preparation after rough-treating which has been forbidden gradually for the healthy reason; second, as the raw chemical materials such as manufacturing soap; third, as the energy resources such as the feedstock of bio-diesel(5,6), preheated and used as fuel for diesel engine(1) or co-gasification with coal(7). The usage of the waste edible oil as the energy resources is promising. For the consciousness of the energy shortage and environmental pollution, seeking new clean and renewable energy becomes a hot world-wide social problem. And the bio-oil is the preferred energy because it is renewable and has low contents of sulfur. The bio-oil production cost is still higher than the petroleum-based fuel. While the waste edible oil with lower raw material cost has the similar molecular weight and chemical structure to bio-oil product. So the waste edible oil instead of the bio-oil to produce the fuel and chemicals is a good choice.

The usage of the waste edible oil as feedstock of bio-diesel (mainly referred fatty acid methyl ester) is fully summarized by Mangesh G(3). All the processes are transesterification reactions with alkali, acid, enzyme or ionic liquid as catalysts, or by the supercritical fluid process without any catalyst. A series of achievements have gotten in transesterification processes. But the production of bio-diesel needs rigorous pretreatment of the feed and the process produces some wastes which still need further treatment for environmental reasons. Moreover the bio-diesel has the problem for high viscosity, high melting point, which is also trouble for the diesel

engine in the cold area. The desired product is just bio-diesel and can not be adjusted according to the market demand. The methods of preheated and used as fuel for diesel engine or co-gasification with coal is not a good method to fully use the waste edible oil. It is important to develop a new technology that can treat the waste edible oil with variant quality to high-value products.

In order to meet this requirement, the waste edible oil downer reactor fluid catalytic cracking process is studied, because from the chemical composition point of view, the waste edible oil is good resource for refineries and chemical plants. It mainly consist of long-chain (about 15-18 carbon atoms in one molecule) fatty acid which is easily to pyrolysis, it is lighter than petroleum without resin and asphaltene, and lower content of sulfur, nitro asphaltum compounds than petroleum. Meanwhile, the technology of fluid catalytic cracking process (FCC) in refinery is fully developed(21) and has less rigorous requirement to feed than the transesterification process, in addition, FCC process can produce the gasoline, diesel and high-value chemical raw material such as propylene. Moreover the distribution of the products can be adjusted according to the market requirement. A series of literatures (8-20) have proved the technology of bio-oil catalytic cracking process feasible. The catalysts are Y, ZSM-5, MCM-41 zeolite catalysts and the reactors are fixed-bed reactor or fluidized-bed reactor. The influences of catalysts and operation conditions on the product distributions are discussed. But all the catalytic cracking processes above are all using the edible oil as the feeds and have high costs. The cottonseed oil and the waste edible oil contain some ingredients which can induce a series of disease and have a relative low cost in the production of fuel. So the objectives of this study is to use non-edible bio-oil: cottonseed oil and the waste edible oil in a downer FCC unit to produce gasoline and diesel, the products distributions and products qualities are also studied.

EXPERIMENTS

1 Feed oil and Catalyst

The waste edible oil (WEO) was obtained from the Benji Company, Beijing in China. The cottonseed oil was obtained from Xinguang Company, Shandong province in China. The vacuum gasoline oil (VGO) was obtained from Jinan Refinery, Shandong province in China. And the chemical and physical properties of the feed oil are shown in Table 1-3.

2 Catalyst

The catalyst is a new FCC catalyst for fluid catalytic cracking process coded as MA-83, developed by Lanzhou Petro-Chemical Institute. It was stream aged at 800 °C for 17hr. The physical and chemical properties of the MA-83 catalyst can be found in Table 4.

Table 1 Properties of Vacuum Gasoline Oil

Properties		
Density 20 C (g/cm ³)		0.8896
Viscosity 80 C(mm ² /s)		8.986
Refractive Index(70 °)		1.47
Carbon Residue (wt%)		0.48
Element composition	C wt%	86.61
	H wt%	12.81
	S mg/L	6
	N mg/L	8.5
Group composition	saturate	69.9%
	aromatics	23.8%
	resin	6.2%
	asphaltene	0.1%

Table 2 Properties of Cottonseed Oil

Properties		
Density 20 C (g/cm ³)		0.91
Acid Value mgKOH/g		1
Saponification Value mgKOH/g		194
Element composition	O wt%	11.5
	S mg/L	6
	N mg/L	8.5
composition	Palmitic (16:0)	28
	Stearic (18:0)	1
	Oleic(18:1)	13
	linolenic	58

Table 3 Properties ofWaste Edible Oil

Properties		
Density 20 C (g/cm ³)		0.92
Acid Value mgKOH/g		124.54
Saponification mgKOH/g		197.27
Element composition	O wt%	12.47
	S mg/L	96
	N mg/L	63
composition	free fatty acid	63
wt%	triglyceride	30
	monoester and diester	7

Table 4 Properties of MA-83 catalyst

Properties		MA-83
Na ₂ O, wt%		0.22
Surface area, m ² /g		261
Pore volume, mL/g		0.38
Apparent density, g/mL		0.74
Attrition index, m%		1.9
MAT, Micro-activity testing		
	800°C×17h	67
Distribution of size V%		
	0-45.8µm	<25
	45.8-111.0µm	< 50
	>111.0µm	< 30

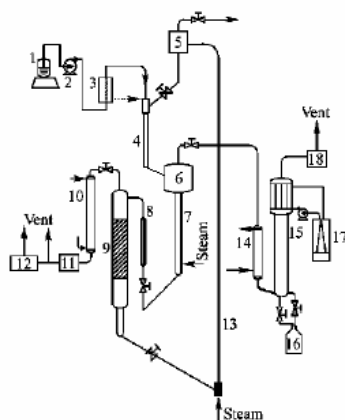
3 Equipment and experimental procedure

The downer FCC experimental apparatus, shown in Figure 1, includes feeding system, reaction-regeneration system and product collector system. The downer reactor is a 1200mm long, 14mm i.d, stainless steel tube placed coaxially in a furnace. The operation specification of this apparatus are as follows: feed rate of oil: 200~1800g/hr, catalyst reserve: 4000~10000g, reaction temperature: 400~700°C, catalyst/oil ratio: 7~30, resident time: 0.6~5s, regeneration temperature: 600~750°C.

4 Product analysis

The cracking gas product was analyzed by GC 1790 with Al₂O₃ packed column and FID detector. The liquid product was separated to gasoline (<200°C), diesel (200°C~360°C) and FCC slurry (>360°C) by ENGLER distillation. The coke yield was obtained by online analyzing the content of CO₂ in the regeneration flue gas and the flux of flue gas. The group composition of gasoline is analyzed by HP-PONA column and PONA-station software developed by China Petroleum University (East China). And the functional group of the feed, gasoline and diesel is analyzed by FT-IR Spectrometer. The composition of the waste edible oil is analyzed by the High Performance Liquid Chromatography (HPLC) and the FT-IR Spectrometer. The

content of sulfur, nitrogen and oxygen in feeds and products are analyzed respectively by microcoulometry, chemiluminescence apparatus and element analyzer.



- | | |
|-------------------------|------------------------------|
| 1 feed reservoir | 2 syringe pump |
| 3 pre-heater | 4 downer |
| 5 catalyst reservoir | 6 gas-solid separator |
| 7 stripping tower | 8 catalyst transporting line |
| 9 regenerator | 10 air cooler |
| 11 flue gas meter | 12 CO ₂ analyzer |
| 13 catalyst riser | 14 cooler |
| 15 gas-liquid separator | 16 liquid collector |
| 17 refrigerator | 18 cracking gas meter |

Figure 1 Schematic diagram of experimental apparatus

RESULTS AND DISCUSSIONS

1 The chemical composition of the waste edible oil

In order to study the process of the waste edible oil fluid catalytic cracking, the feed- waste edible oil should be analyzed. The analysis by FT-IR and HPLC were carried out. The Figure 2 is the IR spectrums of the waste edible oil and the cotton seed oil. The results of the HPLC prove there is much content of free fatty acid in the waste edible oil and the quantitative analysis tells the weight percent of free fatty acid in the waste edible oil 63wt%, the triglyceride 30wt%, and the monoester and diester 7wt%. And

comparing with the IR spectrum of the cotton seed oil, the stretching vibration peaks of the function group C=O (about 1735 cm^{-1}) becomes two peaks between $1700\text{--}1750\text{ cm}^{-1}$ which proves there are maybe two function groups containing C=O in the waste edible oil. From the results, we can obtained that the two function groups containing C=O in the waste edible oil are ester (R_1COOR_2) and carboxyl (RCOOH). The acid value of the waste edible oil was 124.54 mg/gKOH according to the GB 9104.3-1988 method and the weight percent of the free fatty acid is 62.6 wt% with the conversion of the acid value to the content of the free fatty acid which is just accorded with the result of the HPLC. The analysis of the IR, HPLC and the acid value tells that the waste edible oil comprises the free fatty acid and triglyceride mainly.

2 Product distribution

The waste edible oil fluid catalytic cracking process was studied at the experimental equipment just described in 2.3. The operation condition was as that the temperature 500°C , the pressure $1.1 \times 10^5\text{ Pa}$, the resident time 1 second, the ratio of catalyst to oil 12, and MA-83 as the catalyst, which was a new developed FCC catalyst for fluid catalytic cracking process. In order to compare the products with those producing with the VGO or vegetable oil as feed, the VGO and the cotton seed oil fluid catalytic cracking processes are also studied at the same operational condition. The products were analyzed by the methods described in 2.4 and the product distribution is shown in Table 5 and Table 6.

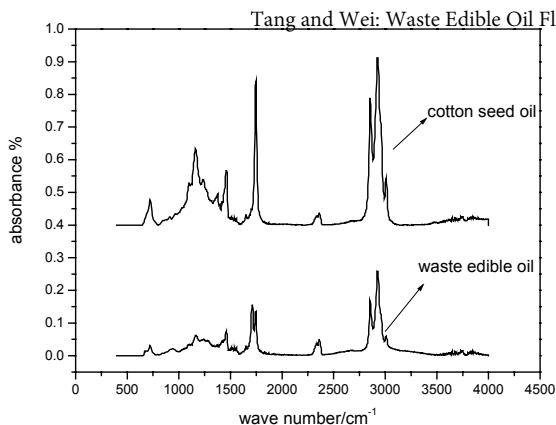


Figure 2 IR spectrum of the feeds

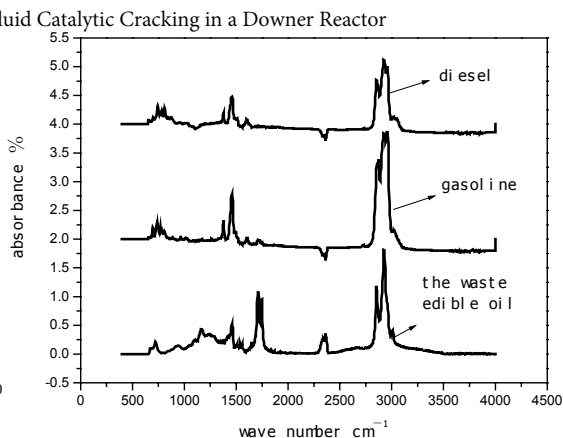


Figure 3. IR spectrum of gasoline and diesel.

The similar product distributions are obtained with the waste edible oil or the cottonseed oil as the feed in the fluid catalytic cracking process. The yield of dry gas is only about 0.5-0.7wt%; the liquefied petroleum gas (LPG) 10.26-11wt%; the gasoline 36-38wt%; the diesel 24-27wt%; the coke 9-11%; and the yield of water is about 14 wt% because of the high oxygen content in the bio-oil. Although the compositions of the waste edible oil and the cotton seed oil are different: the waste edible oil consists of the free fatty acid in 63 wt%, the triglyceride 30 wt%, the monoester and diester 7 wt%; and in cotton seed oil the triglyceride 100 wt%, there are the same function groups of $(\text{CH}_2)_m$ and $(-\text{COO}-)$ which obey the same rules when catalytic cracking. From the product distributions and analysis, the conclusion is obtained that the fluid catalytic cracking process with the waste edible oil instead of the cottonseed oil as feed is feasible and also the achievements in the vegetable oil catalytic cracking process can be used for reference in the waste edible oil catalytic cracking process.

The direct comparisons of the Product Distributions between the waste edible oil (WEO), cottonseed oil and the vacuum gasoline oil (VGO) is not reasonable for the WEO and Cottonseed oil contain about 12% oxygen which can't convert to desired products and only the hydrocarbons can convert to desired products. So in Table 6 the comparison of product distributions between WEO, cottonseed oil, and VGO, the product distributions of the waste edible oil and cotton seed oil are treated by take out the oxygen from the feeds and products. The yields of dry gas and LPG are the same; and the yield of gasoline with the WEO as the feed is lower and the diesel is higher than with the VGO as the feed. And the yield of slurry with the WEO as the feed is lower than with the VGO as the feed which may due to the fact that VGO contains resin which is easy to convert to slurry. And the coke yield in the cracking of bio-oil is relatively high, may for the reason of the high acidity in bio-oil leading to easily coke generation, and the MA-83 catalyst, which is designed to have high conversion but relatively high coke yield.

According to the calculation of the oxygen conservation between the feed (waste edible oil) and the products, the oxygen in feed almost converts to water in products. And the conclusion is also proved by the FT-IR spectrums of products shown in Figure 3. In the FT-IR spectrums of gasoline and diesel, the stretching vibration peaks of the function group $\text{C}=\text{O}$ (about 1735cm^{-1}) and the function group $\text{C}-\text{O}$ ($1250-1000\text{cm}^{-1}$) (22) are all weak. Those FT-IR spectrums further prove that the

gasoline and diesel contain trace oxygen and the oxygen in feed almost exists in the product with the form of water.

Table 5 Comparisons of Product Distributions between Waste Edible Oil and Cottonseed Oil

	waste edible oil	Cotton seed oil
Temperature/C	500	500
Pressure/MPa	0.1	0.1
Resident time/s	1	1
Catalyst/oil	12	12
Product distributions wt%		
Dry gas	0.65	0.61
LPG	10.26	11
Gasoline	36.38	38.72
Diesel oil	26.96	24.09
Slurry	1.78	1.456
Coke	10.8	9.243
Water	13.17	14.87
Conversion %	100	100
Desired product yield%	73.56	73.81

Table 6 Comparisons of Product Distributions Between Bio-oil and VGO

	WEO	Cotton seed oil	VGO
Temperature /C	500	500	500
Pressure /MPa	0.1	0.1	0.1
the resident time/s	1	1	1
Catalyst/oil	12	12	12
Product distributions wt%			
Dry gas	0.788	0.689	0.51
LPG	13.83	12.43	13.5
Gasoline	44.58	43.75	48.8
Diesel oil	28.26	27.22	26.4
Slurry	1.93	1.64	2.68
Coke	9.89	10.44	7.97

Conversion=(1-unreacted feeds)/all the feeds

Desired product yield=(LPG+ gasoline+ diesel)/ all the feeds

3 The Product Analysis

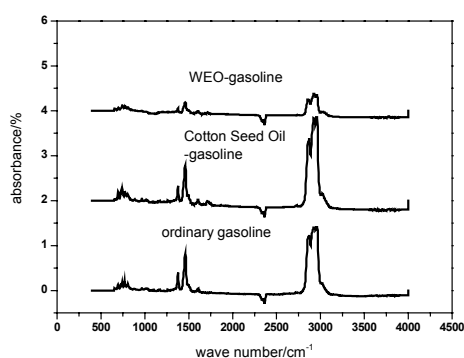
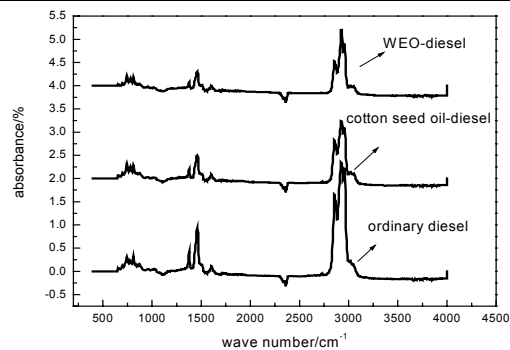
The product's property which is vital if the waste edible oil fluid catalytic cracking process could be industrialized was analyzed. The group composition of gasoline is analyzed by HP-PONA column and PONA-station software developed by China Petroleum University (East China), as shown in Table 7. The group composition of gasoline produced with the VGO and the waste edible oil is similar.

And the FT-IR analysis to gasoline and diesel were also carried out and the results are shown in Figures 4 and 5. The FT-IR Spectrums of gasoline (Figure4) and diesel (Figure5) indicate that the gasoline and diesel produced with the waste edible oil as feed have the similar function groups to the gasoline and diesel from petroleum-based feed.

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Table 7 The Group Composition of Gasoline

Feed	the group composition of gasoline (PONA)			
	paraffin %	olefin %	naphthene %	aromatics %
VGO	34.74	33.80	13.9	20.12
waste edible oil	35.9	31.10	12.26	19.64

**Figure 4 IR spectrum of the gasoline****Figure 5 IR spectrum of the diesel**

The sulfur content in gasoline and diesel is continuously reduced by regulations to lower levels. How to reduce the sulfur content in fuel becomes a vital problem in refinery to meet the regulations. The sulfur is very low in bio-oil in comparison with petroleum, which will lead to low sulfur content in gasoline and diesel produced by bio-oil, the sulfur content of gasoline and diesel produced by the waste edible oil was analyzed, as shown in Table 8. The sulfur content of gasoline is 41 $\mu\text{g/g}$ and can meet the requirement of the World Wide Fuel Charter II (<200 $\mu\text{g/g}$) and Europe IV (50 $\mu\text{g/g}$). The sulfur content of diesel is 117 $\mu\text{g/g}$ and also can meet the requirement of the World Wide Fuel Charter II (<300 $\mu\text{g/g}$) and Europe III (350 200 $\mu\text{g/g}$).

Table 8 The Sulfur Content of Gasoline and Diesel

	Feeds		the content of sulfur (mg/L)
	gasoline	diesel	
gasoline	Waste edible oil		41
	Petroleum-based		About 200-1500
Diesel	Waste edible oil		117
	Petroleum-based		About 700-2700

CONCLUSIONS

The waste edible oil normally contains 60-70% free fatty acid and 20-30% triglyceride, which depends on its source. And the fluid catalytic cracking process with the waste edible oil as feed can produce clean fuel and high-value chemical raw materials, both of which are urgently needed in energy market, and it should also been pointed out that the product distribution could be adjusted according to the market requirement. Used as fuel, the desired products, gasoline and diesel produced by the waste edible oil fluid catalytic cracking process hold the same property as the gasoline and diesel from petroleum-based fuel, because they have the similar molecular weight and chemical structure. Moreover, the gasoline and diesel through this process belong to the environmental-friendly products for they have trace content of sulfur. In a word, the waste edible oil fluid catalytic cracking, providing the fuel and high-value chemical material, shows attractive application prospect in waste reusing field and energy field, with both economic and environmental benefit.

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